**Supporting information**

# Low temperature catalytic oxidative coupling of methane in an electric field over Ce-W-O catalyst system

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## Materials

A stock solution of 1.0 M of V(V) was prepared by dissolving 9.186 g of $V_2O_5$ and 6.194 g of NaOH in 100 mL of water (0.5 M $V_2O_5$/1.5M NaOH). Other reagents were of analytical grade and were used as received.

## Preparations of tetrabutylammonium (TBA) salt of Keggin-type HPAs

### *Preparation of $(TBA)_3[PW_{12}O_{40}]$ (denoted as TBA-$PW_{12}$)*

An aqueous solutions of 1.0 M $Na_2WO_4$ (5 mL), conc. HCl (4.2 mL), and 1.0 M $NaH_2PO_4$ solution (0.5 mL) were poured into 100 mL vessel in the order, and diluted with 100 mL of water. The resultant solution was aged at 353 K for 2 days in static. After the resulting clear solution had been cooled to room temperature, three equivalents (0.484 g) of tetrabutylammonium (TBA) bromide, $[CH_3(CH_2)_3]_4NBr$, was added to solution. After solution stirred at room temperature for 30 min, the resultant white solid was filtered off, washed with distilled water (50 mL) and ethanol (20 mL), and dried at 393 K overnight.

IR(KBr): $\nu$ = 1079 (m), 975 (s), 895 (s), 814 (s) $cm^{-1}$.

### *Preparation of $(TBA)_4[PW_{11}V_1O_{40}]$ (denoted as TBA-$PW_{11}V_1$)*

An aqueous solutions of 1.0 M $Na_2WO_4$ (5 mL), 0.5 M $V_2O_5$/1.5M NaOH (0.5 mL), conc. HCl (4.2 mL), and 1.0 M $NaH_2PO_4$ solution (0.5 mL) were poured into 100 mL vessel in the order, and diluted with 100 mL of water. The resultant solution was aged at 353 K for 2 days in static. After the resulting yellow solution had been cooled to room temperature, four equivalents (0.645 g) of tetrabutylammonium (TBA) bromide, $[CH_3(CH_2)_3]_4NBr$, was added to solution. After solution stirred at room temperature for

30 min, the resultant yellow solid was filtered off, washed with distilled water (50 mL) and ethanol (20 mL), and dried at 393 K overnight.

IR(KBr): ν = 1095 (w), 1069 (w), 962 (s), 889 (m), 808 (vs) $cm^{-1}$.

***Preparation of $(TBA)_5[PW_{10}V_2O_{40}]$ (denoted as TBA-$PW_{10}V_2$)***

An aqueous solutions of 1.0 M $Na_2WO_4$ (5 mL), 0.5 M $V_2O_5$/1.5M NaOH (2.0 mL), conc. HCl (4.2 mL), and 1.0 M $NaH_2PO_4$ solution (0.5 mL) were poured into 100 mL vessel in the order, and diluted with 100 mL of water. The resultant solution was aged at 353 K for 2 days in static. After the resulting orange solution had been cooled to room temperature, five equivalents (0.806 g) of tetrabutylammonium (TBA) bromide, $[CH_3(CH_2)_3]_4NBr$, was added to solution. After solution stirred at room temperature for 30 min, the resultant orange solid was filtered off, washed with distilled water (50 mL) and ethanol (20 mL), and dried at 393 K overnight.

IR(KBr): ν = 1095(w), 1063 (w), 960 (s), 889 (m), 808 (vs) $cm^{-1}$.

Table S1 Catalytic activities over 40 wt%TBA-$PW_{12}O_{40}/CeO_2$ in various temperatures without electric field[a]

| Condition | External temp. / K | $CH_4$ Conv. / % | $O_2$ Conv. / % | $C_2$ Sel. / % | $C_2$ Yield / % |
|---|---|---|---|---|---|
| without EF | 573 | 0.1 | 0.7 | 0.0 | 0.0 |
| | 673 | 0.1 | 2.1 | 0.0 | 0.0 |
| | 773 | 0.4 | 4.2 | 0.0 | 0.0 |
| | 873 | 1.3 | 3.8 | 0.0 | 0.0 |
| | 973 | 1.3 | 5.9 | 0.0 | 0.0 |
| | 1073 | 5.0 | 14.8 | 3.5 | 0.2 |

[a] Feed gas $CH_4$:$O_2$:Ar = 25:15:60 SCCM, catalyst weight: 100 mg, furnace temperature: 573-1073 K

Table S2 Effect of input current on catalytic activity over 40 wt%TBA-$PW_{12}O_{40}/CeO_2$ in the electric field[a]

| Current / mA | $T_{tc}$[b] / K | Voltage / kV | $CH_4$ Conv. / % | $O_2$ Conv. / % | $C_2$ Sel. / % | $C_2$ Yield / % | Field intensity / V $mm^{-1}$ | Faradaic number / - |
|---|---|---|---|---|---|---|---|---|
| 3.0 | 689 | 1.3 | 14.9 | 20.6 | 43.4 | 6.4 | 260 | 83.3 |
| 5.0 | 772 | 0.8 | 32.5 | 40.1 | 40.0 | 13.0 | 160 | 109 |
| 7.0 | 863 | 0.7 | 52.8 | 63.3 | 32.0 | 16.9 | 140 | 127 |

[a] Feed gas $CH_4$:$O_2$:Ar = 25:15:60 SCCM, input current: 3.0-7.0 mA, catalyst weight: 100 mg, furnace temperature: 423 K

[b] Catalyst bed temperature measured by a thermocouple

Table S3 Catalytic activities over 40 wt%TBA-HPAs/$CeO_2$ in the electric field[a]

| Catalysts | $T_{tc}$[b] / K | Voltage / kV | $CH_4$ Conv. / % | $O_2$ Conv. / % | $C_2$ Sel. / % | $C_2$ Yield / % | Field intensity / V $mm^{-1}$ | Faradaic number / - |
|---|---|---|---|---|---|---|---|---|
| TBA-$PW_{12}/CeO_2$ | 772 | 0.8 | 32.5 | 40.1 | 40.0 | 13.0 | 160 | 109 |
| TBA-$PW_{11}V_1/CeO_2$ | 754 | 0.8 | 26.4 | 34.7 | 31.8 | 8.4 | 136 | 83.4 |
| TBA-$PW_{10}V_2/CeO_2$ | 708 | 0.7 | 25.5 | 34.2 | 31.4 | 8.0 | 130 | 81.1 |
| $CeO_2$ | 675 | 0.1 | 28.2 | 100 | 0.2 | 0.1 | 20 | 93.1 |

[a] Feed gas $CH_4$:$O_2$:Ar = 25:15:60 SCCM, input current: 5.0 mA, catalyst weight: 100 mg, furnace temperature: 423 K

[b] Catalyst bed temperature measured by a thermocouple

TBA-HPAs: TBA-$PW_{12-x}V_xO_{40}$ (x = 0~2)

Table S4 Catalytic activities over various oxide catalysts in the electric field (power fixing)[a]

| Catalysts | $T_{tc}$[b] / K | Current / mA | Power / W | $CH_4$ Conv. / % | $O_2$ Conv. / % | $C_2$ Sel. / % | $C_2$ Yield / % | Field intensity / V $mm^{-1}$ | Faradaic number / - |
|---|---|---|---|---|---|---|---|---|---|
| TBA-$PW_{12}/CeO_2$ | 595 | 1.5 | 2.6 | 5.8 | 14.5 | 43.7 | 2.6 | 315 | 61.4 |
| $Ce_2(WO_4)_3/CeO_2$ | 649 | 3.0 | 2.7 | 13.6 | 18.5 | 39.0 | 5.3 | 225 | 73.9 |
| $WO_3/CeO_2$ | 634 | 3.0 | 2.4 | 14.3 | 20.8 | 32.4 | 4.6 | 145 | 74.0 |
| $Ce_2(WO_4)_3$ | 659 | 3.0 | 2.1 | 9.7 | 11.6 | 41.2 | 4.0 | 189 | 53.3 |
| $WO_3$ | 586 | 20.0 | 2.0 | 0.2 | 1.7 | 0.0 | 0.0 | 29 | 0.1 |

[a] Feed gas $CH_4$:$O_2$:Ar = 25:15:60 SCCM, input current: 1.5, 3.0, 20.0 mA, catalyst weight: 100 mg, furnace temperature: 423 K

[b] Catalyst bed temperature measured by a thermocouple

Table S5 Catalytic activities over various oxide catalysts in the electric field (catalyst bed temperature fixing)[a]

| Catalysts | $T_{tc}$[c] / K | Voltage / kV | $CH_4$ Conv. / % | $O_2$ Conv. / % | $C_2$ Sel. / % | $C_2$ Yield / % | Field intensity / V $mm^{-1}$ | Faradaic number / - |
|---|---|---|---|---|---|---|---|---|
| TBA-$PW_{12}/CeO_2$ | 689 | 1.3 | 14.9 | 20.6 | 43.4 | 6.4 | 260 | 83.3 |
| $Ce_2(WO_4)_3/CeO_2$ | 649 | 0.9 | 13.6 | 18.5 | 39.0 | 5.3 | 225 | 73.9 |
| $WO_3/CeO_2$ | 634 | 0.8 | 14.3 | 20.8 | 32.4 | 4.6 | 145 | 74.0 |
| $Ce_2(WO_4)_3$ | 659 | 0.7 | 9.7 | 11.6 | 41.2 | 4.0 | 189 | 53.3 |
| $WO_3$ [b] | 684 | 0.1 | 0.0 | 14.3 | 0.0 | 0.0 | 29 | 0.0 |

[a] Feed gas $CH_4$:$O_2$:Ar = 25:15:60 SCCM, input current: 3.0 mA, catalyst weight: 100 mg, furnace temperature: 423 K ([b] 673 K)

[c] Catalyst bed temperature measured by a thermocouple

Table S6 Temperature dependency over $Ce_2(WO_4)_3/CeO_2$ in the electric field (power fixing)[a]

| Furnace temp. / K | $T_{tc}$[b] / K | Current / mA | Voltage / kV | Power / W | $CH_4$ Conv. / % | $O_2$ Conv. / % | $C_2$ Sel. / % | $C_2$ Yield / % | Field intensity / V $mm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 423 | 649 | 3.0 | 0.9 | 2.7 | 13.6 | 18.5 | 39.0 | 5.3 | 225 |
| 673 | 830 | 5.0 | 0.5 | 2.5 | 16.2 | 36.9 | 33.7 | 5.5 | 122 |
| 873 | 993 | 10.0 | 0.3 | 3.0 | 18.7 | 47.1 | 18.0 | 3.4 | 77 |

[a] Feed gas $CH_4$:$O_2$:Ar = 25:15:60 SCCM, input current: 3.0, 5.0, 10.0 mA, catalyst weight: 100 mg, furnace temperature: 423, 673, 873 K

[b] Catalyst bed temperature measured by a thermocouple

Table S7 Result of periodic operation test (after 2 and 12 min from $CH_4$ supply) over $Ce_2(WO_4)_3/CeO_2$ without electric field at 1073 K[a]

| Cycle number / - | Time / min | $CH_4$ Conv. / % | $C_2$ Sel. / % | $CO_x$ Sel. / % | $C_2$ Yield / % |
|---|---|---|---|---|---|
| 1 | 2 | 0.17 | 11.6 | 88.4 | 0.02 |
| | 12 | 0.39 | 4.1 | 95.9 | 0.02 |
| 2 | 2 | 0.18 | 8.3 | 91.7 | 0.02 |
| | 12 | 0.37 | 4.5 | 95.5 | 0.02 |
| 3 | 2 | 0.20 | 8.6 | 91.4 | 0.02 |
| | 12 | 0.39 | 4.4 | 95.6 | 0.02 |
| 4 | 2 | 0.22 | 7.7 | 92.3 | 0.02 |
| | 12 | 0.40 | 4.3 | 95.7 | 0.02 |
| 5 | 2 | 0.23 | 8.0 | 92.0 | 0.02 |
| | 12 | 0.44 | 4.1 | 95.9 | 0.02 |

[a] Feed gas: $O_2$:Ar = 15:60 SCCM, $CH_4$:Ar = 25:60 SCCM, catalyst weight: 100 mg, furnace temperature: 1073 K

Table S8 Results of *in-situ* Raman over $Ce_2(WO_4)_3/CeO_2$ with and without electric field

| | Conditions | Voltage / kV | Wavenumber / $cm^{-1}$ $Ce_2(WO_4)_3$ | |
|---|---|---|---|---|
| | | | $W^{I}$-O | $W^{II}$-O |
| (a) | inert (RT) | - | 948 | 929 |
| (b) | without EF (air, 603-703 K) | - | 945 | 927 |
| (c) | with EF (air, 6.0 mA) | 0.69 | 937 | 922 |
| (d) | with EF ($CH_4$, 6.0 mA) | 0.73 | 938 | 922 |
| (e) | with EF ($CH_4$+$O_2$, 6.0 mA) | 0.67 | 938 | 922 |
| (f) | without EF after (e) | - | 947 | 930 |

Table S9 Result of curve fitting over $Ce_2(WO_4)_3/CeO_2$ catalysts in various state[a]

| Conditions | bond | CN | R / A | dE / eV | DW / $A^2$ | R-factor |
|---|---|---|---|---|---|---|
| as-made | W-O | 1.05 | 1.730 | 3.652 | 0.0040 | 0.047 |
| | W-O | | 1.768 | | | |
| | W-O | | 1.812 | | | |
| | W-O | | 1.818 | | | |
| | W-O | | 2.197 | | | |
| after $O_2$ supply in periodic operation test | W-O | 1.01 | 1.706 | -1.233 | 0.0038 | 0.050 |
| | W-O | | 1.743 | | | |
| | W-O | | 1.787 | | | |
| | W-O | | 1.792 | | | |
| | W-O | | 2.166 | | | |
| after 1 cycle in periodic operation test | W-O | 0.84 | 1.753 | 8.669 | 0.0035 | 0.047 |
| | W-O | | 1.790 | | | |
| | W-O | | 1.836 | | | |
| | W-O | | 1.841 | | | |
| | W-O | | 2.225 | | | |
| after reaction with electric field | W-O | 0.88 | 1.709 | -2.286 | 0.0040 | 0.014 |
| | W-O | | 1.746 | | | |
| | W-O | | 1.790 | | | |
| | W-O | | 1.795 | | | |
| | W-O | | 2.170 | | | |

[a] k- range: 3-11Å, R-range: 1-2.3 Å

Table S10 BET surface area of various catalysts as made and after reaction with electric field

| Catalysts | BET surface area / $m^2\ g^{-1}$ | |
|---|---|---|
| | as made | after reaction |
| $TBA\text{-}PW_{12}/CeO_2$ | 52.1 | 5.6 |
| $Ce_2(WO_4)_3/CeO_2$ | 3.6 | 3.2 |
| $WO_3/CeO_2$ | 90.1 | 18.6 |
| $Ce_2(WO_4)_3$ | 1.0 | 0.7 |

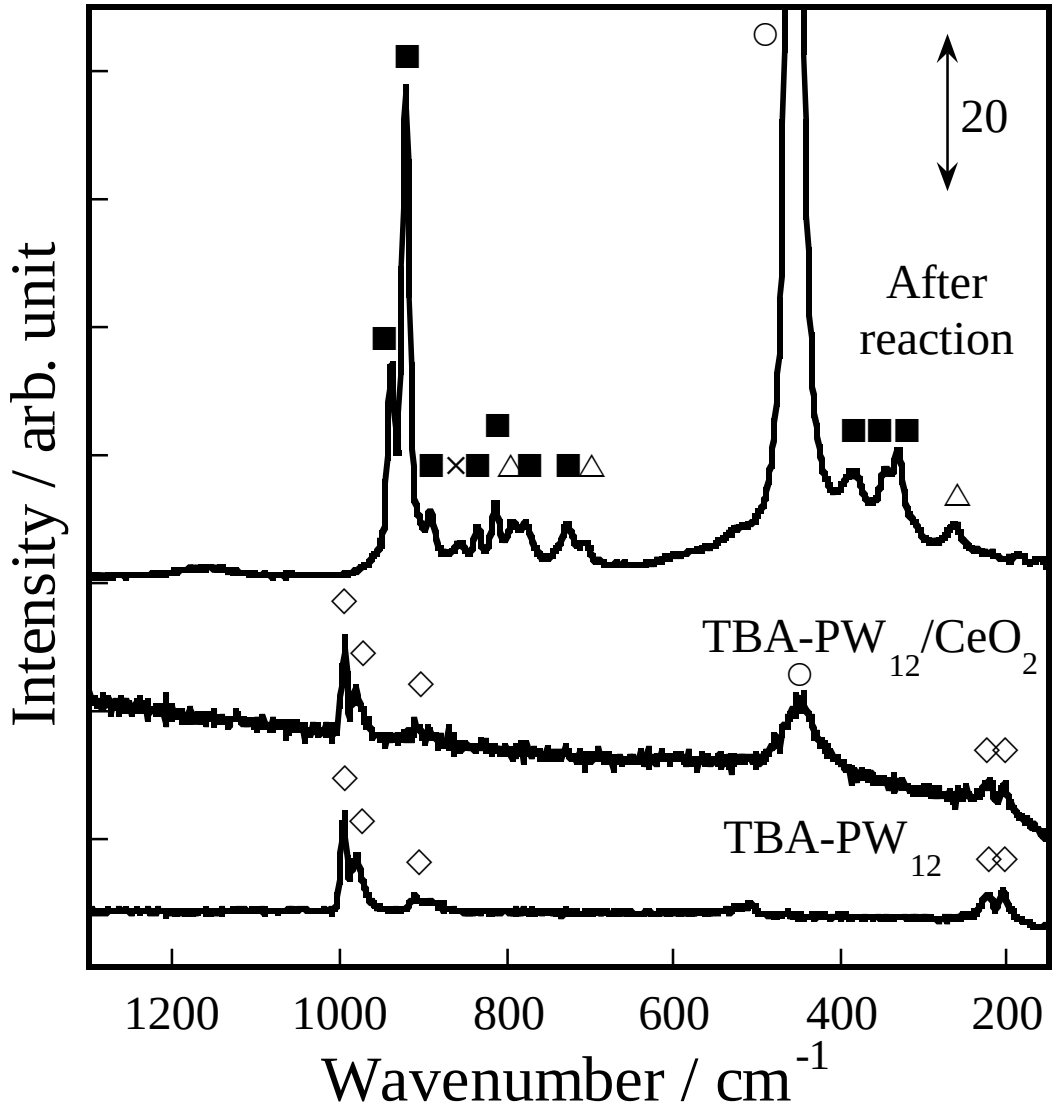


Fig. S1 Raman spectra of TBA-$PW_{12}O_{40}$ and 40 wt%TBA-$PW_{12}O_{40}$/$CeO_2$ before and after reaction with electric field.

○: $CeO_2$, ◇: $[PW_{12}O_{40}]^{3-}$, △: $WO_3$, ■: $Ce_2(WO_4)_3$, ×: Unidentified

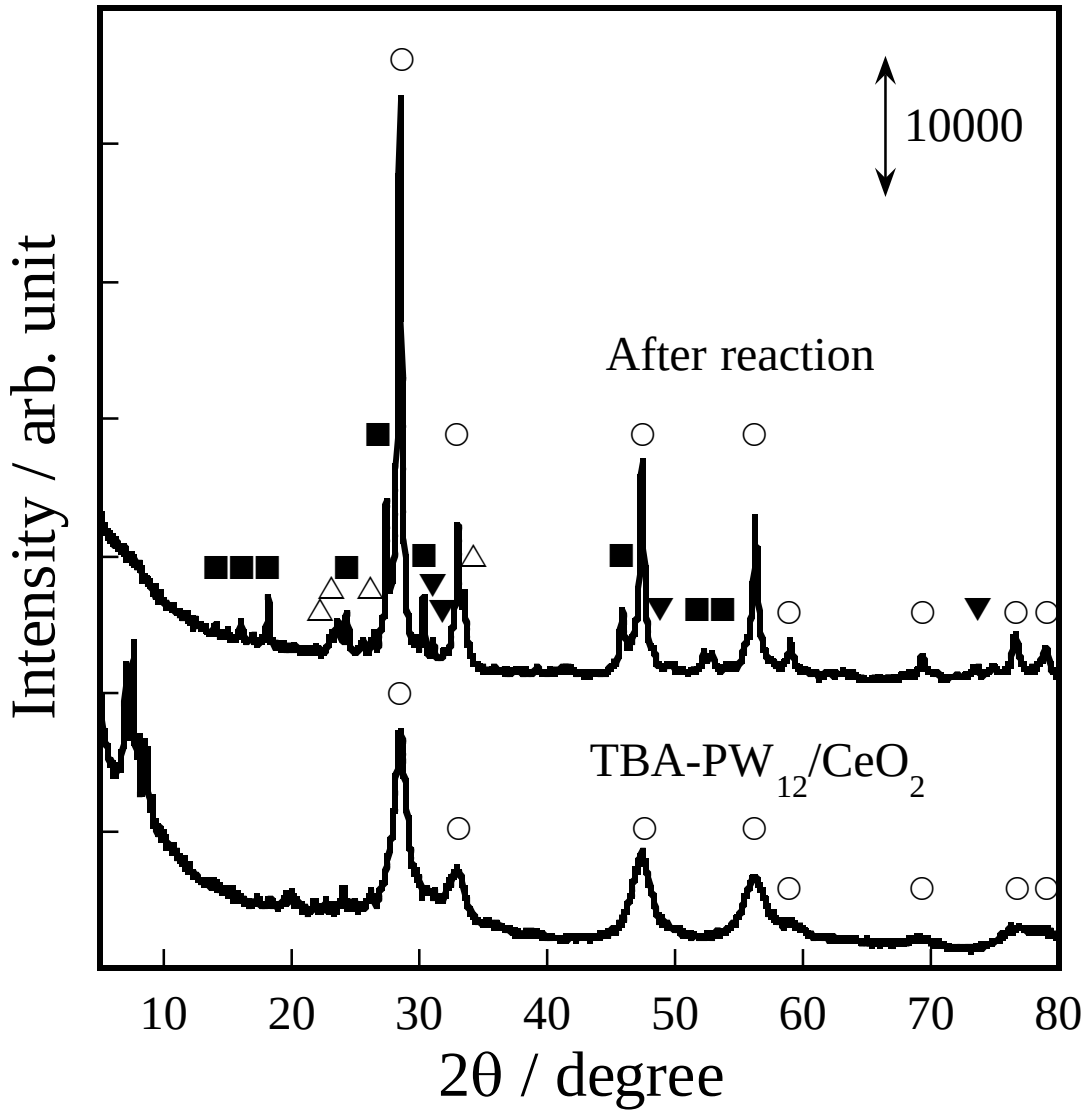


Fig. S2 XRD patterns of 40 wt%TBA-$PW_{12}O_{40}/CeO_2$ before and after reaction with electric field.

○: $CeO_2$, △: $WO_3$, ■: $Ce_2(WO_4)_3$, ▼: $Ce_2WO_6$

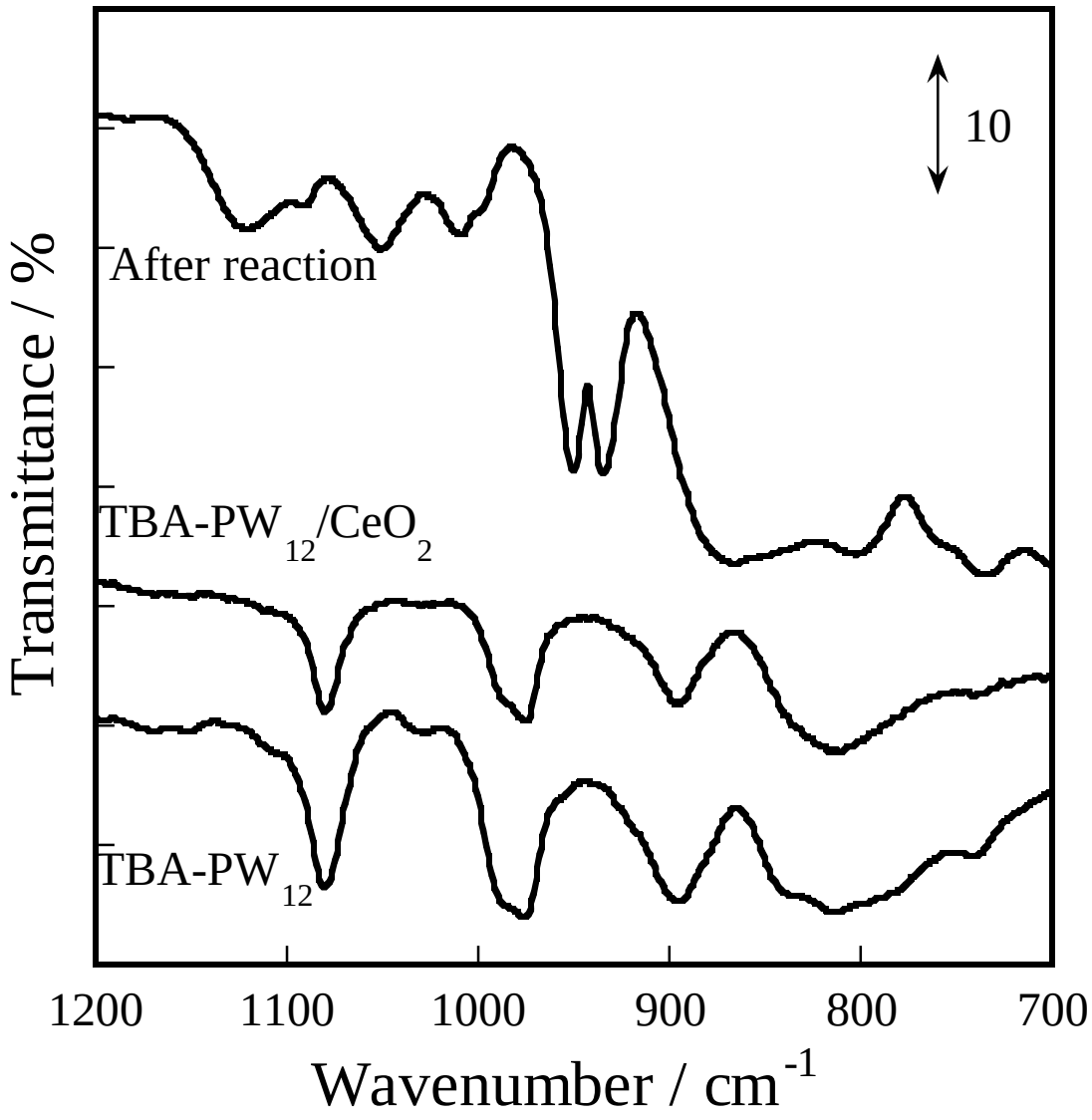


Fig. S3 IR spectra of TBA-$PW_{12}O_{40}$ and 40 wt%TBA-$PW_{12}O_{40}$/$CeO_2$ before and after reaction with electric field.

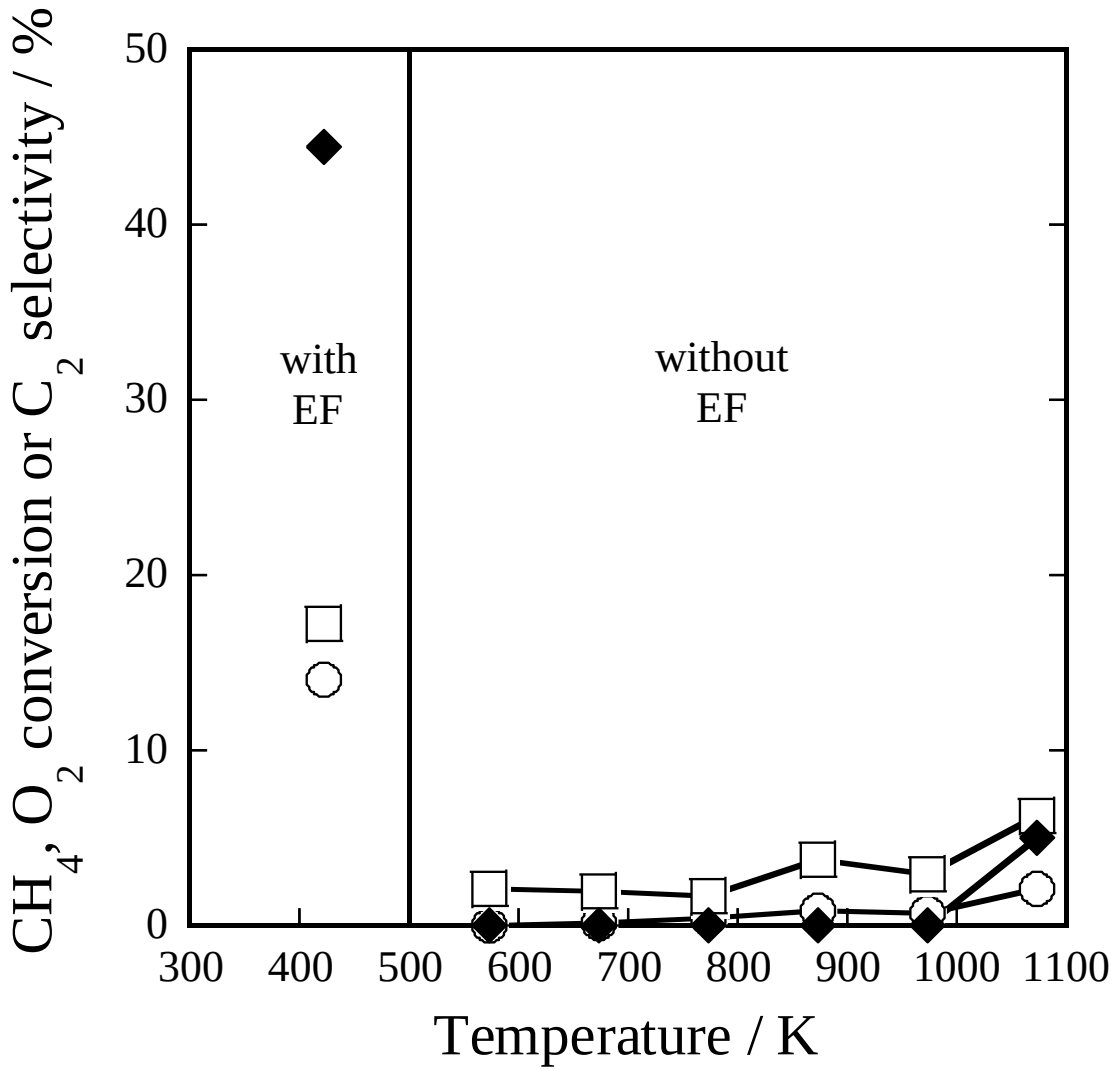


Fig. S4 Catalytic activity in the conventional reaction (573-1073 K) over 40 wt% TBA-$PW_{12}O_{40}/CeO_2$ after the reaction with electric field (423 K, 3.0 mA, 10 min). ○: $CH_4$ Conv., □: $O_2$ Conv., ◆: $C_2$ Sel.

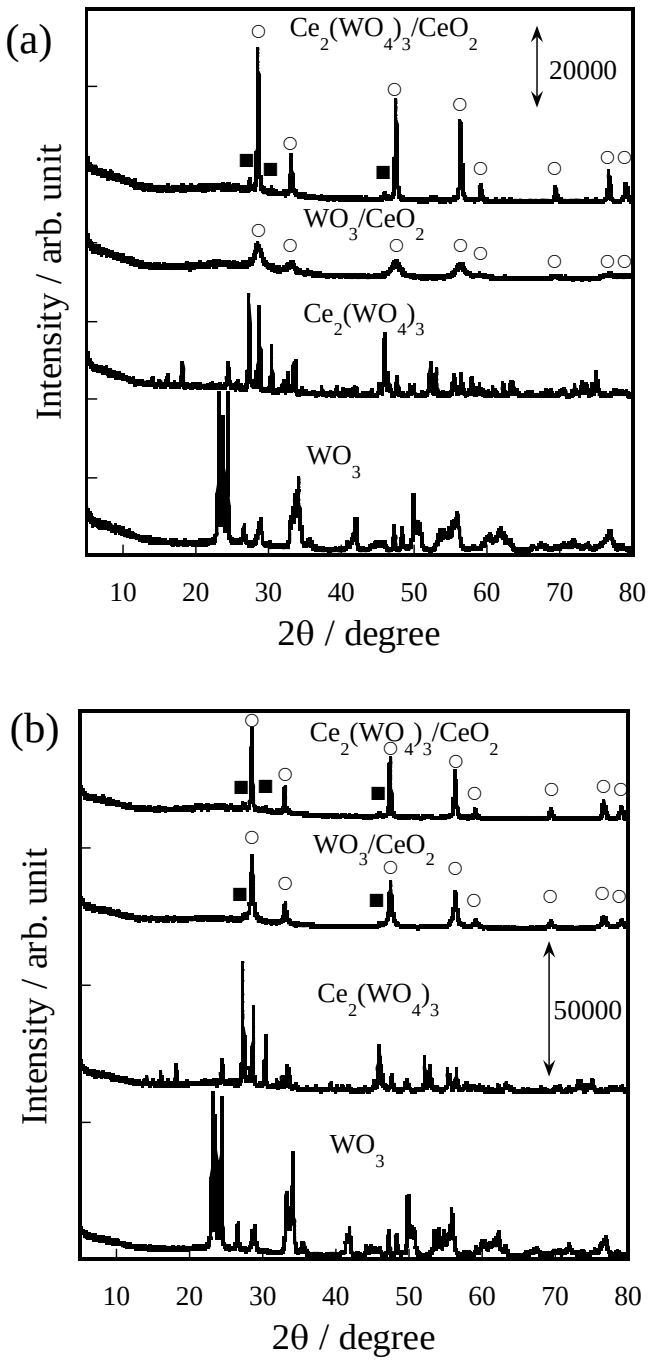


Fig. S5 XRD patterns of various oxide catalysts.
(a) as-made, (b) after reaction with electric field
○: $CeO_2$, ■: $Ce_2(WO_4)_3$

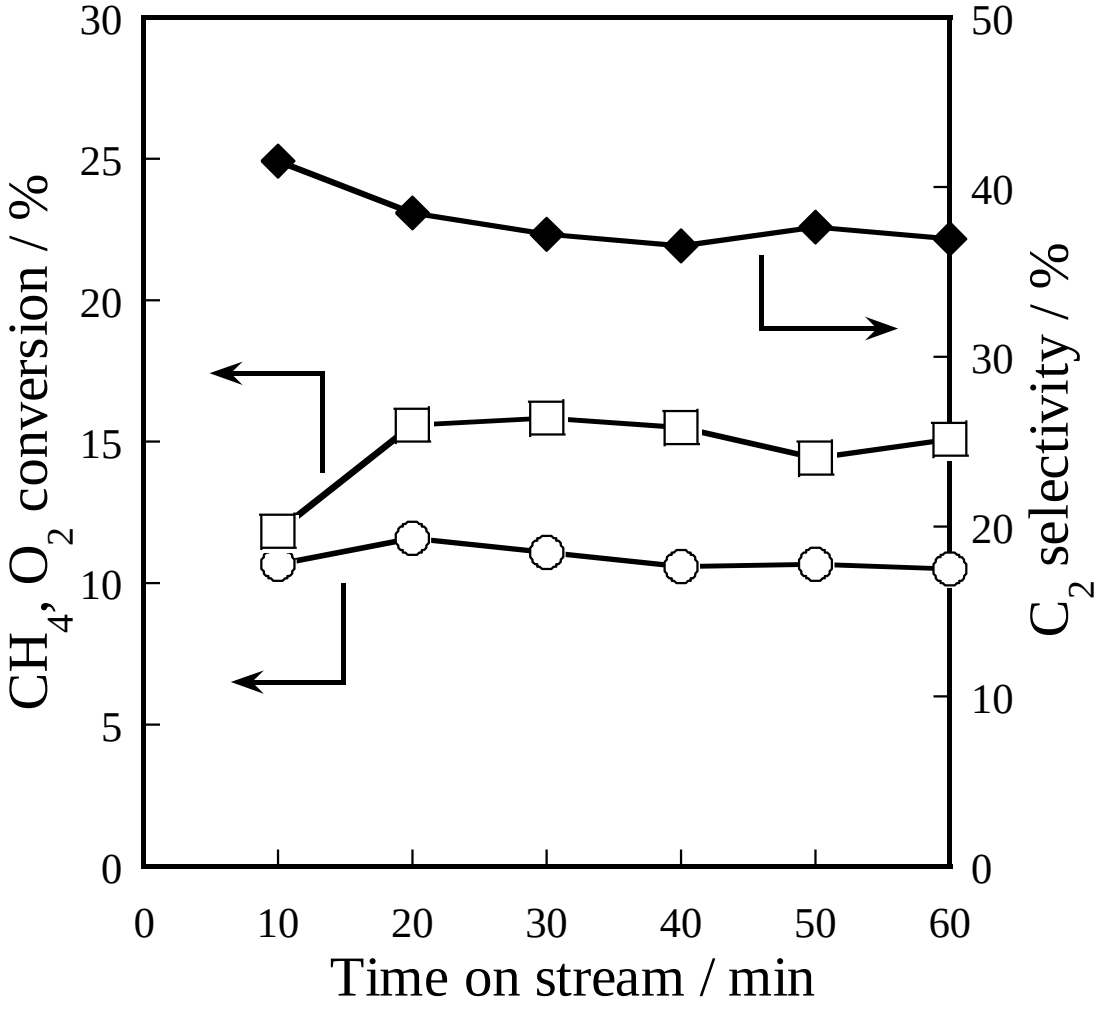


Fig. S6 Time course of the $CH_4$ and $O_2$ conversion and $C_2$ selectivity for OCM over $Ce_2(WO_4)_3/CeO_2$ in the electric field (423 K, 3.0 mA).
○: $CH_4$ Conv., □: $O_2$ Conv., ◆: $C_2$ Sel.

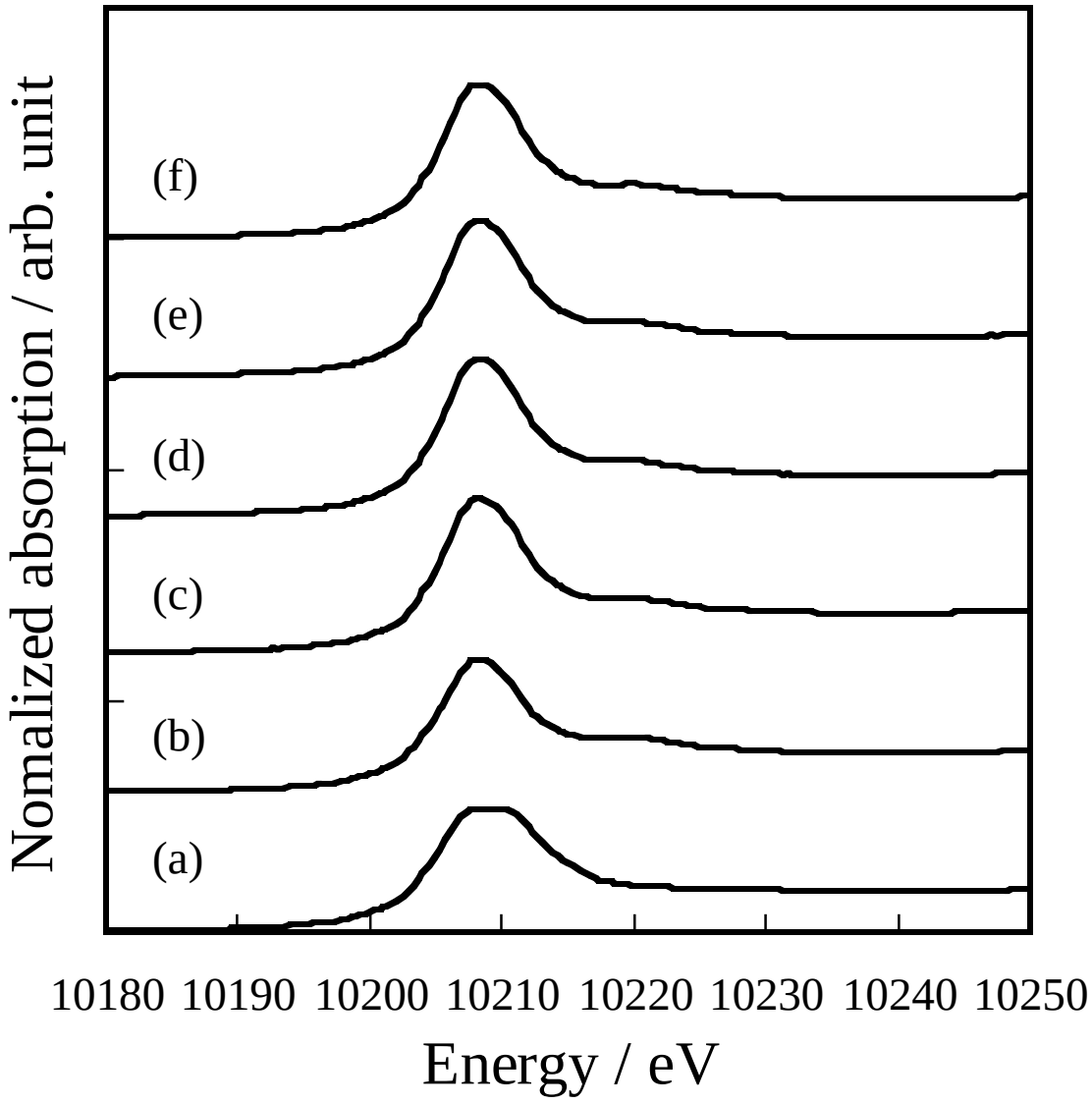


Fig. S7 XANES spectra at W $L_3$-edge over $WO_3$, $Ce_2(WO_4)_3$ and $Ce_2(WO_4)_3/CeO_2$ catalysts in various state.

(a) $WO_3$, (b) $Ce_2(WO_4)_3$, (c) $Ce_2(WO_4)_3/CeO_2$ as-made, (d) $Ce_2(WO_4)_3/CeO_2$ after $O_2$ supply in periodic operation test, (e) $Ce_2(WO_4)_3/CeO_2$ after 1 cycle in periodic operation test, (f) $Ce_2(WO_4)_3/CeO_2$ after reaction with electric field

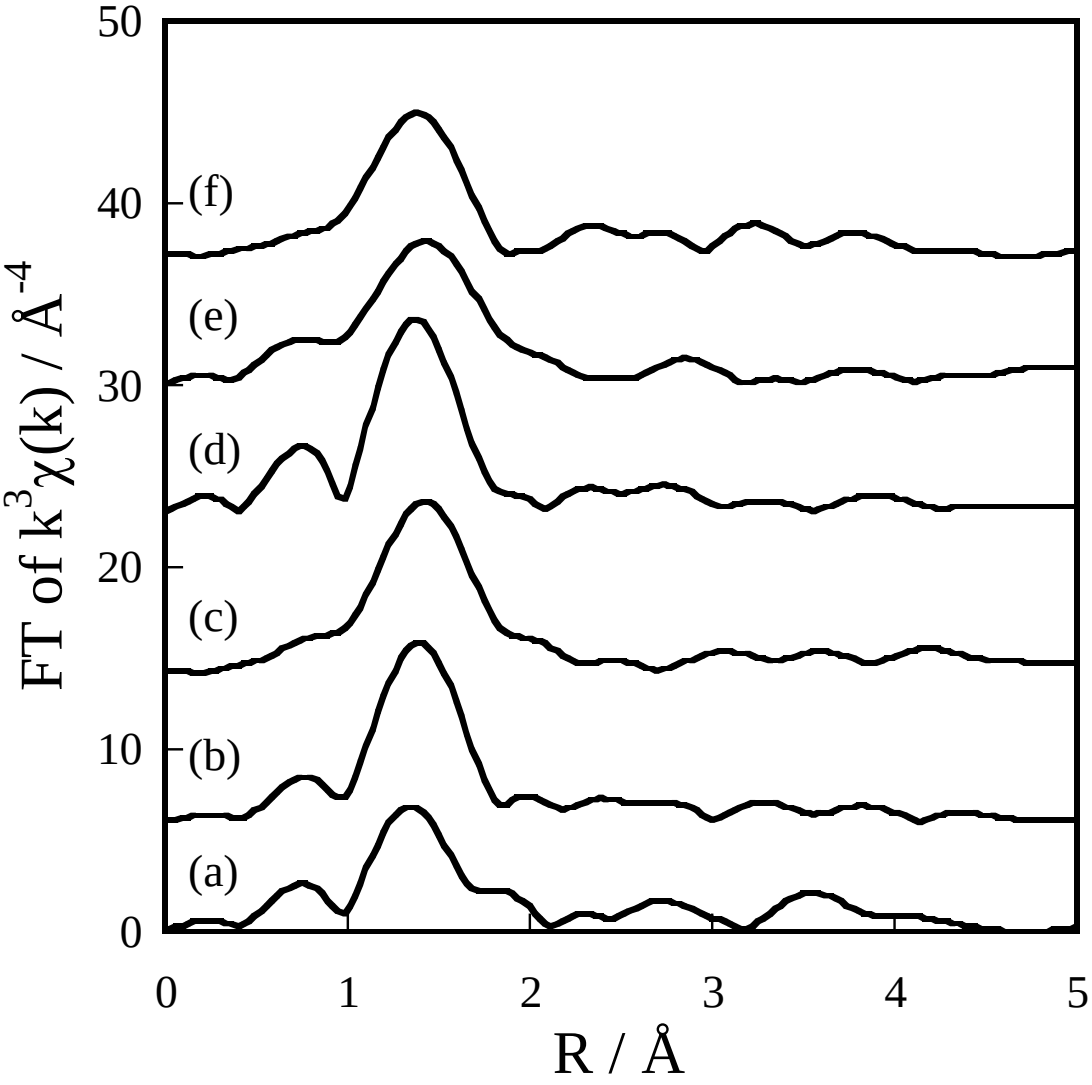


Fig. S8 EXAFS spectra at W $L_3$-edge over $WO_3$, $Ce_2(WO_4)_3$ and $Ce_2(WO_4)_3/CeO_2$ catalysts in various state.

(a) $WO_3$, (b) $Ce_2(WO_4)_3$, (c) $Ce_2(WO_4)_3/CeO_2$ as-made, (d) $Ce_2(WO_4)_3/CeO_2$ after $O_2$ supply in periodic operation test, (e) $Ce_2(WO_4)_3/CeO_2$ after 1 cycle in periodic operation test, (f) $Ce_2(WO_4)_3/CeO_2$ after reaction with electric field

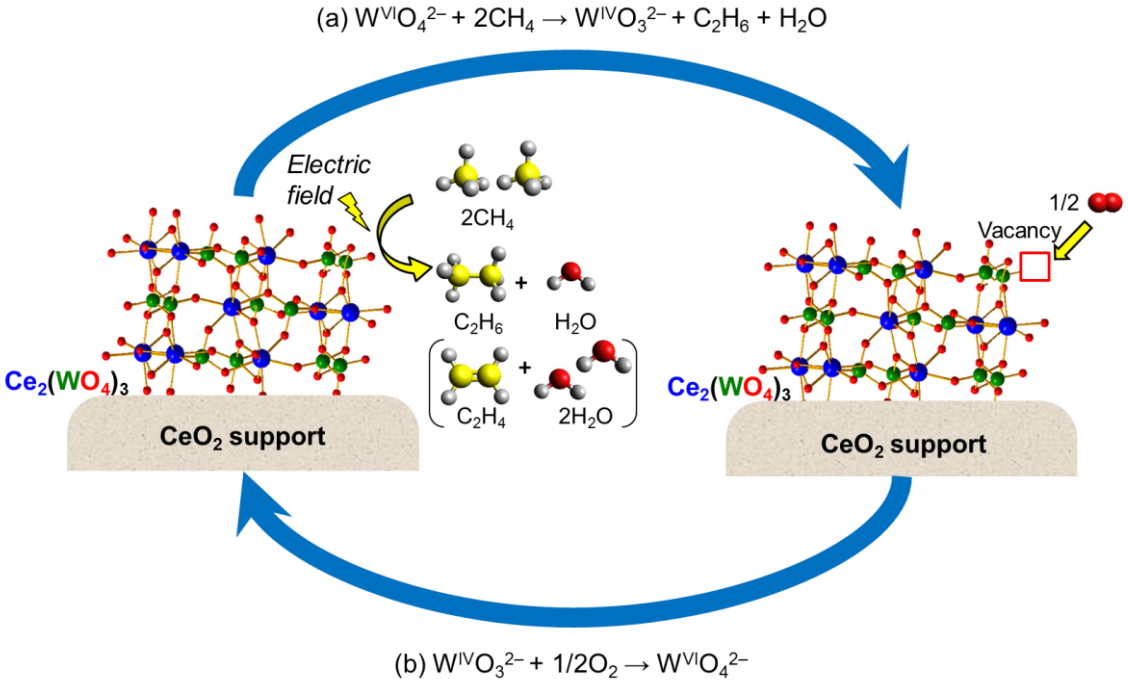


Fig. S9 Possible reaction mechanism of OCM over $Ce_2(WO_4)_3/CeO_2$ catalyst in the electric field:

(a) OCM occurred using lattice oxygen of $Ce_2(WO_4)_3$ (short W–O bond in distorted $WO_4$ unit); (b) Reproduction of lattice oxygen by gas-phase oxygen.

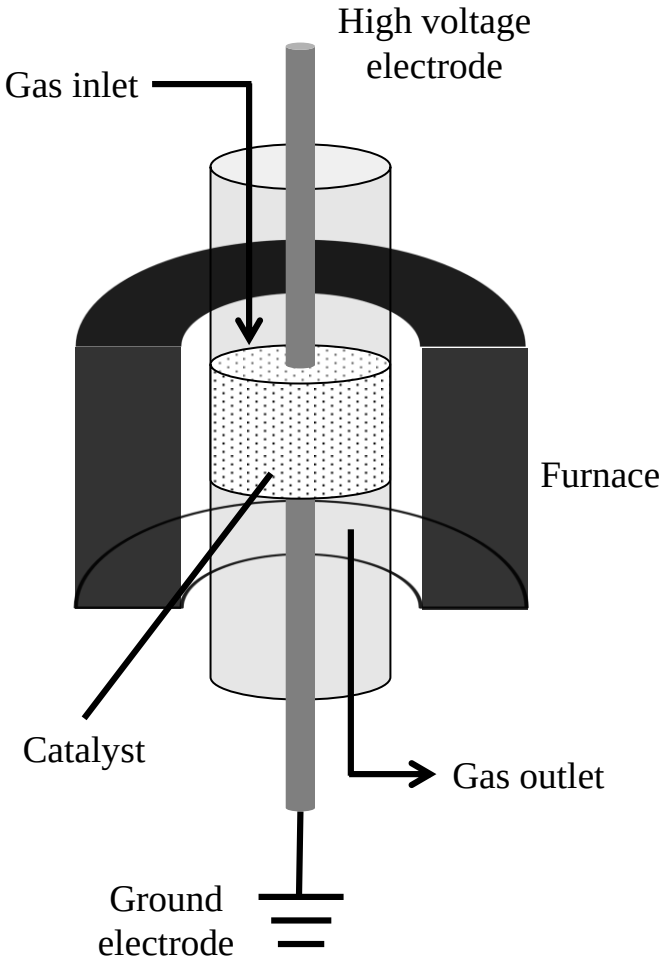


Fig. S10 Schematic diagram of reactor.

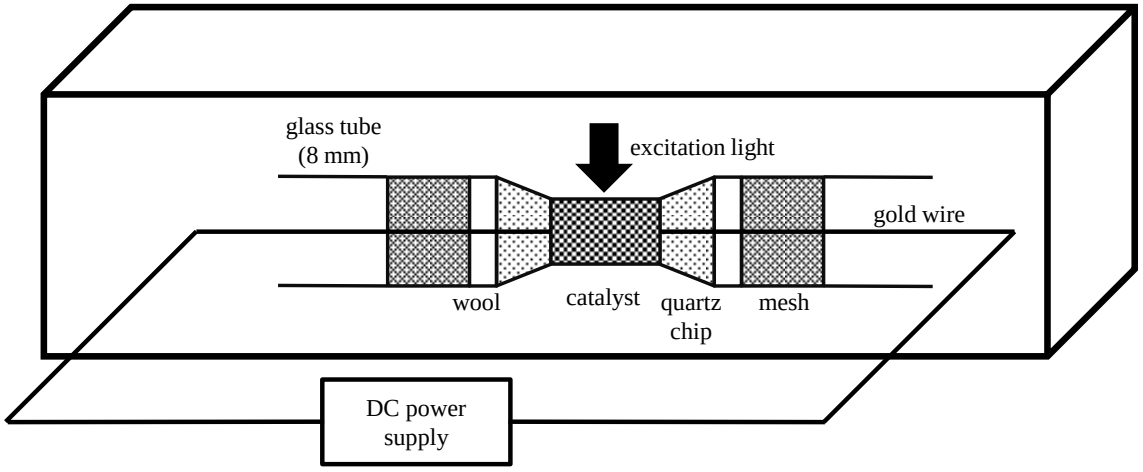


Fig. S11 Schematic diagram of reactor for *in-situ* Raman.